Hydrogen–vacancy interaction in W and Mo

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The hydrogen–vacancy interaction in W and Mo was investigated by applying the perturbed angular correlation technique, using the isotope ^{111}In as a probe. Hydrogen trapping at InV$_2$ manifests itself as a change of the vacancy-induced quadrupole frequency. We have observed trapping of up to two H atoms. The binding energies for the first H atom are 1.07(2) eV in Mo and 1.16(2) eV in W. These results are close to the values calculated with the effective-medium theory. The frequency shifts are both negative and amount to a few Mrad/s per trapped H atom. Contrary to the theoretical predictions, the binding energies for the second H atom differ strongly: 0.44(3) eV in Mo and 0.99(2) eV in W. The corresponding frequency shifts have opposite signs. Therefore, the lattice positions of the first H atom in Mo and W are similar, while those of the second H atom must be completely different.

1. Introduction

We report on an experiment in which we applied the PAC technique, using the isotope ^{111}In as a probe, to monitor the number of H atoms trapped at a vacancy in bcc Mo and W. We used the complex InV$_2$ as a unique and reproducible trap; it gives rise to the well-known quadrupole frequencies $\omega_0 = 117$ Mrad/s in Mo and $\omega_0 = 133$ Mrad/s in W. The annealing treatments required to produce this complex have been described in refs. [1,2] for Mo, and in refs. [3–5] for W. We could determine the implanted H dose very accurately by injecting the H atoms with the aid of a low-energy ion gun. The maximum energy transferred to the host-lattice atoms was less than the displacement energy and, therefore, no further damage was introduced in the samples.

2. Experimental results

The polycrystalline samples were prepared by implanting 50 keV [111]In$^+$ ions to a dose of less than 10^{12} cm^{-2}. The implanted W samples were annealed at 750 K in order to create the complex InV$_2$, and subsequently postimplanted at 300 K with 1 keV H$_2$ molecules, corresponding to 500 eV H$^+$ ions. In the case of Mo, it is not possible to choose an annealing temperature at which only the complex InV$_2$ is

stable. We pre-annealed the molybdenum foils, therefore, at 485 K, at which temperature the fractions of InV_2, InV_3 and InV_4 take their maximum values. The situation in the case of Mo is even more complicated because the quadrupole frequency corresponding with InV_4 depends strongly on the sample temperature; at 80 K the Fourier peaks due to InV_2 and InV_4 nearly coincide. On the other hand, exploratory experiments indicated that H atoms trapped at InV_2 may detrap at a temperature as low as 200 K. The Mo samples were, therefore, doped at 170 K, at which temperature the contributions from InV_2 and InV_4 in the frequency spectrum can be well distinguished.

We studied the hydrogen–vacancy interaction by carefully monitoring the position of the Fourier peak that corresponds with InV_2, as a function of H dose. In the case of W, the frequency corresponding with the InV_2 defect changes from 133 via 127 to 121 Mrad/s, with increasing hydrogen dose, indicating the formation of at least two different defect structures; on further implantation of hydrogen the frequency did not change by more than 0.5 Mrad/s. In the case of Mo, however, the frequency first decreases from the initial value of 117 to 114 Mrad/s and then, at higher hydrogen doses, increases to about 118 Mrad/s. The zero asymmetry parameter turned out not to be affected by the H atoms.

In order to study the stability of the H-decorated defects, annealing sequences were performed at temperatures from 100–600 K (figs. 1 and 2). Two recovery stages are easily recognized in each case. The contributions of InV_2H_n ($n = 0, 1, 2$) in the Fourier spectrum cannot be resolved. Each frequency value was, therefore, determined by analyzing selected spectra in which the corresponding H-decorated complex formed the dominant component.

The interpretation of the observations is obvious. With increasing hydrogen dose, InV_2 is successively decorated with one and two H atoms, according to the reactions in $InV_2 + 2H \rightarrow InV_2H + H \rightarrow InV_2H_2$. At higher temperatures apparently the reverse reactions occur.
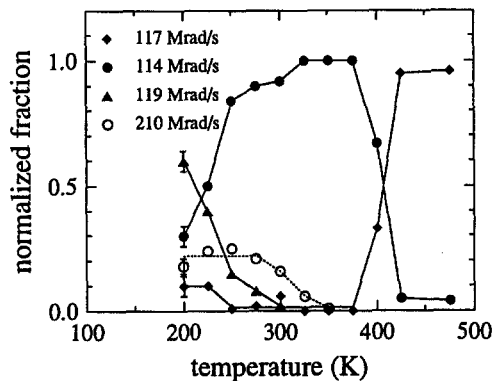

Fig. 1. Defect fractions for InV_2H_n ($n = 0, 1, 2$) in Mo, as a function of the annealing temperature. The 210 Mrad/s component corresponds to a bubble-like feature.
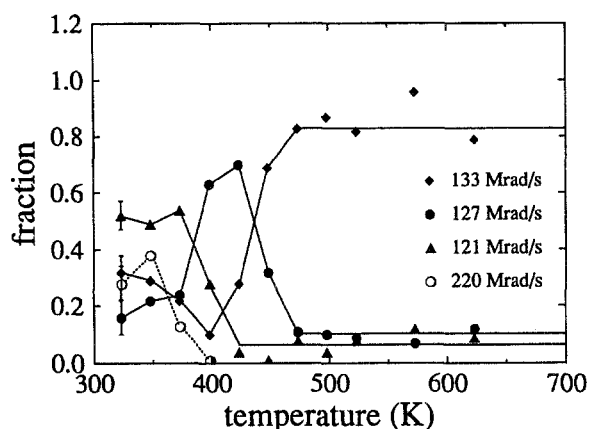
Fig. 2. Defect fractions for InV_2H_n ($n = 0$, 1, 2) in W, as a function of the annealing temperature. The 220 Mrad/s component corresponds to a bubble-like feature.

We define the dissociation temperature, T_d, as the temperature at which the defect fraction is reduced by 50%. It is related to the dissociation energy, E_d, by the expression $E_d = kT_d \ln(\nu t / \ln 2)$, where $\nu = 2 \times 10^{14}$ s^{-1} is the attempt frequency and $t = 900$ s is the annealing time. The binding energies were obtained by subtracting the hydrogen migration energy. The derived values are collected in table 1. The upper limit for the binding energy of the next H atom is determined by the fact that under the experimental conditions no more than two H atoms are trapped.

In the high-dose regime, additional Fourier power was observed in the frequency region 210–220 Mrad/s, which we attribute to bubble-like features. The corresponding hydrogen binding energies are 0.72 eV in Mo and 0.91(2) eV in W.

3. Conclusions

Hydrogen trapping at InV_2 manifests itself as a small but measurable shift of the vacancy-induced quadrupole frequency. The shift turned out to be only a few Mrad/s per trapped H atom; it may be positive as well as negative. Trapping of hydrogen was observed by monitoring the shift of the quadrupole frequency;

Table 1
H–vacancy binding energies for the first, second and next H atom. All values in eV.

Metal	First H atom	Second H atom	Next H atom
Mo [a]	1.07(3)	0.44(3)	<0.25
W [b]	1.16(2)	0.99(2)	<0.7

[a] Assuming a hydrogen migration energy of 0.35 eV.
[b] Assuming a hydrogen migration energy of 0.39 eV.

detrapping of hydrogen was observed by measuring the annealing behaviour of the different frequency components.

The binding energies in Mo and W for the first H atom are approximately equal and close to the values calculated with the effective-medium theory [6,7]. Our result for Mo agrees with the value 1.03 eV obtained by deuterium depth-profiling [8], but disagrees with the value 1.4 eV obtained in positron-lifetime experiments [9]. The frequency shifts are both negative.

Contrary to the theoretical predictions, the binding energies for the second H atom differ largely. Our result for Mo is considerably smaller than the value 0.80 eV deduced from deuterium depth-profiles [8]. The corresponding frequency shifts have opposite signs. Therefore, the lattice positions of the first H atom in Mo and W are similar, while those of the second H atom must be completely different.

Acknowledgement

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